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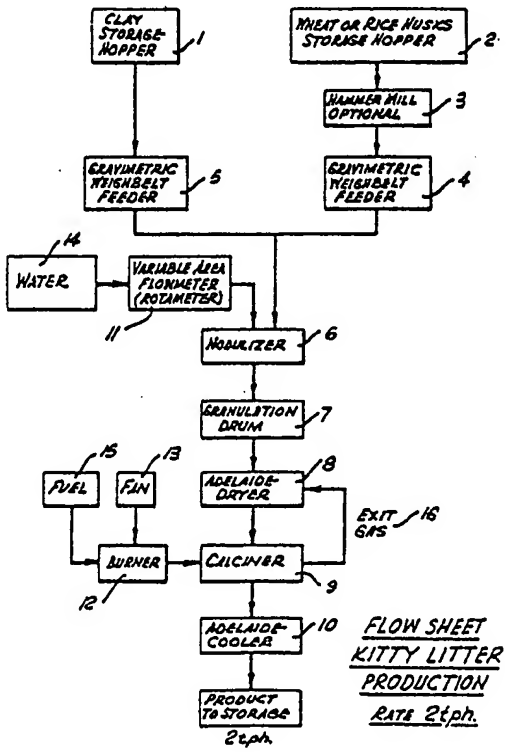
(54) Title: ABSORBENT CLAY

(57) Abstract

An absorbent useful as a 'pet litter' or industrial liquid absorbent is made by mixing clay with cellulosic material such as rice hulls or wheat dust, pelletizing the mixture, drying the resultant pellets and heating the pellets to a temperature of from 550°C to 1100°C.



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Title: "ABSORBENT CLAY"

Technical Field of the Invention

This invention relates to a method of manufacturing an absorbent composition.

Many different materials are employed to absorb oil spills and chemical wastes, or as carriers for insecticides and also as fillers in rubber products, paints and plastics. The most useful absorbents are those that are less costly to make, possess a higher absorbency of both hydrophobic and hydrophillic substances and have a lower tendency to form dust. Such absorbents have a wide range of application.

An increasing quantity of absorbent materials is used in so-called "Pet Litter" products for absorbing urine and other liquid waste.

Background Art

U.S. Patent 3,059,615 describes an animal litter manufactured by acidifying cellulosic materials such as corn cob, grits or cereal hulls with a view to rendering the cellulosic material more absorbent.

A number of absorbent compositions have been proposed in which absorbent binders such as clays or limestone are

combined with fillers available in large quantities at low cost such as rice hulls, corn cobs, flyash, sawdust, peanut hulls, or the like (U.S. Patents 3,735,734, 3,921,581, 3,983,842, 4,258,660).

However the products hitherto available have either been more costly or less effective than is desired.

An object of the present invention is to manufacture an absorbent material at low cost by very simple means. Preferred embodiments of the invention are suitable for use as a "pet litter".

Disclosure of the Invention

According to one aspect the invention consists in method of manufacture of an absorbent composition comprising the steps of: mixing clay with cellulosic material, pelletizing the mixture, drying the resultant pellets, and heating the pellets to a temperature of from 550°C to 1100°C.

Brief Description of the Drawings

Various embodiments of the invention will now be described by way of example only with reference to the accompanying drawings wherein:

Figure 1 is a graph showing the crush strength of pellets of various compositions according to the invention.

Figure 2 shows the water absorption of pellets according to the invention.

Figure 3 is a graph showing the crushing strength of pellets prepared with the addition of sodium carbonate according to the invention.

Figure 4 is a schematic flow chart illustrating a method according to the invention.

Description of Preferred Embodiment

Compositions according to the invention desireably utilize a clay of generally uniform quality as a starting material.

The clay is combined with a cellulosic material such as the hulls of the rice grain or rice husks, which are a by-product of rice milling and therefore cheap and readily obtainable or wheat dust or grain dust which are available as low cost waste products.

It is preferable to mill the clay to a fine particle size since this facilitates mixing with the rice hulls or wheat dust which are also preferably milled to a fine particle size.

Adding the clay and rice or wheat together with water in a pelletizer or agglomerator develops small pellets which can then be dried and baked. The quantity of water added is desireably the minimum required for aggregation.

The pellets are subsequently dried and then heated to above 550°C. It is believed that during this step the cellulosic material is not only carbonized but fully combusted.

In choosing a suitable clay or binder it is preferable to perform tests at first crushing, milling and screening the raw clay; mixing with sufficient water the facilitate agglomeration; agglomeration to form pellets; oven drying at 100°C for one to two hours; firing the

pellets at 850°C for say 3 hours in a muffle furnace and then; cooling the pellets. The water absorbency of the resultant milled product is measured and those clays found to have a high percentage of absorption of liquids and a low level of dust after meat treatment are preferred for use in the invention.

The following examples of various embodiments of the invention will better describe the invention.

In one series of examples a white burning clay was milled to a maximum particle size of 300 microns, and rice hulls or wheat dust was milled to a maximum particle size of 150 microns. The clay and the rice hulls or wheat dust were each then mixed in various proportions by mechanical means, about 20% water by weight was added and the resulting mixture formed into pellets of up to 6 mm in diameter by means of an agglomerator or pelletising machine. The pellets were then passed to a dryer which was the first section of a tunnel kiln at a temperature of up to 100°C. Once dried to a moisture content of less than 4% the pellets continued to be passed through the kiln but the temperature of the second section of the kiln was between 800 and 1000°C. The pellets were held in the kiln for about one hour.

The ratio of wheat dust to clay and rice hulls to clay was 14:86, 21:79, 28:72 and 35:65 respectively. Calcination temperatures were 800°C, 900°C and 1000°C.

To determine the tendency to form dust, crushing

tests were conducted by individually subjecting the pellets to a force applied by metal plunger with the results shown in Table I.

TABLE I

TYPE OF ADDITIVE	RICE HULLS A				WHEAT DUST B			
ADDITIVE %	14	21	28	35	14	21	28	35
CLAY %	86	79	72	65	86	79	72	65
	MEAN CRUSHING STRENGTH OF GRANULE (grams/3mm pellet)							
CALCINATION TEMP.								
800°C	210	60	41	32	42	34	35	20
900°C	380	380	155	51	113	25	33	15
1000°C	383	170	85	35	310	182	26	11

The results of these tests are illustrated graphically in Figure 1 in which crushing strength in grams/3mm granule (pellet) is shown on the ordinate axis and percentage of additive A (Rice Hulls) or B (Wheatdust) on clay is shown on the coordinate axis at various calcination temperatures.

In order to test absorptivity the pellets were placed in Gooch crucibles with glass fibre pads. The crucibles were filled with distilled water and the water was allowed to percolate through the pellets. After draining this step was repeated.

Following the second draining the excess water was removed using a water tap venturi vacuum connection on a

low pressure. The crucibles plus contents were then weighed with the result, as shown in Table 2.

Table 2

ABSORBTIVITY OF GRANULES

TYPE OF ADDITIVE	RICE HULLS A				WHEAT DUST B			
ADDITIVE %	14	21	28	35	14	21	28	35
CLAY %	86	79	72	65	80	79	72	65
CALCINATION TEMP.	WATER ABSORPTION (grams/kg)							
800°C	404	541	671	873	582	700	845	1124
900°C	454	547	674	796	561	694	877	1126
1000°C	460	571	658	892	565	640	803	893

The results of Table 2 are illustrated graphically in Figure 2 which shows the water absorption in grams/100 grams of pellets on the ordinate axis and which shows the percentage by weight of rice hulls (A) or Wheat dust (B) added to the clay on the coordinate axis.

In other embodiments the ratio of clay to rice hulls or wheat dust has been varied from between 80%:20% by weight to 60%:40% by weight and particle sizes of clay and rice hulls have been varied between 75 and 600 microns. For finer particle size provides a more effective product but is more costly to obtain.

After drying of the pelletized mixture the hardened pellets have been exposed to kiln temperatures of from 550° to 850°C for from 3 to 1 hours, respectively.

Temperatures of up to 1100°C may be employed.

It appears desirable that the firing temperatures must be high enough to combust all the carbon in the rice hulls or wheat dust.

Pellets manufactured in accordance with the invention compared according to the U.S. Interim Federal Specification for Sweeping Compounds, P.S.O. 008656(GSA-FSS) with commercially available pet litter pellets, showed the following results:

TABLE 3

	Apparent Density (llb/Cubic ft)	Oil Absorption (ml/g)	Water Absorption (ml/g)
Pet Litter	51.9	0.64	0.66
"Katlit"	33.8	0.75	0.75
"Diatomite"	32.8	0.86	0.97
"Pet Litter"	43.8	0.60	0.60
Absorbant According to invention based on white clay	41.1	0.98	1.06

In further experiments the addition of wheat dust was found to give surprizingly better results than other cellulosic materials. The high absorbency of the pellets attributed to the fact that as the carbon is burned off in the kiln during the firing steps the organic silica skeleton of the rice hulls is left intact and an enhanced porosity is obtained. Grasses such as rice and wheat and other graminaceous plants absorb soluble silica from the soil which is deposited in insoluble form in the cell

tissues. The amount of silica absorbed is a function of the transpiration.

Investigations into the preparation of a clay/rice husk product indicated that agglomeration was the preferable method of combining the two. Agglomeration produced a more consistent particle size range of the pellets with a rounded surface and therefore maximum surface area as compared with angular or crusted aggregates. Little or no dust was produced and no pressure was applied which would have increased the density.

As shown in Table 4 the addition of from 1 to 4% of a carbonate is beneficial. A number of samples were prepared, each consisting of clay (560 g), wheat dust (240g) and water 510g. Various quantities of sodium carbonate (from 0-32g) were dissolved in the water.

The products were pelletized, dried at 105°C and then calcined at 800, 900 and 1000°C respectively for 2 hrs.

Granule crushing strength tests were conducted as previously described with the result shown in Table 4.

TABLE 4
CRUSHING STRENGTH OF KITTY LITTER

GRANULE CRUSHING STRENGTH (grams)
n = 20 Granules (-2.80 +2.00 mm)

CALCIUM TEMP.	% Na_2CO_3 ADDED			
	0	1	2	4
800°C	approx. 1	11.6 ± 3	8.1 ± 3	24.4 ± 6
900°C	21.9 ± 8	42 ± 20	116.5 ±40	131.7 ± 28
1000°C	54.8 ± 18	154 ± 25	230.7 ±54	481 ±108

These results are illustrated graphically in Figure 3.

The results indicate that the addition of sodium carbonate was beneficial. Moisture absorptivity tests on products made with 4% sodium carbonate yielded an average moisture absorbtivity of in the range from 550 g/kg - 850 g/kg.

By way of example of a method for manufacture of pellets according to the invention a flow sheet is shown in Figure 4.

Clay is fed from storage hopper 1 to a gravimetric weight belt feeder 5. Wheat dust or rice hulls from a hopper 2 are optionally ground by hammer mill 3 and fed to gravimetric weightbelt feeder 4.

The weighed, and optionally ground, rice hulls or wheat and clay feedstocks are combined in nodulizer 6 together with water 14 metered via a flowmeter 11. The nodulizer properly incorporates the rice hulls or wheat dust into the clay and water and is preferably a twinshaft paddle mixer.

The mixture is then treated in granulation drum 7 pellets or granules which are transferred to a drier 8, for example an "Adelaide Dryer".

The dried pellets proceed to calciner 9 which is fueled by a burner 12 boosted by fan 13 and supplied with fuel 15. Exit gas 16 from calciner 9 is used to heat dryer 8.

The calcined product passes to cooler 10 prior to packaging.

The cooling step is only needed if it is desired to package the product within 24 hrs.

To an extent which will be apparent to those skilled in the art from the teaching hereof other similar finely divided fibrous materials such as peanut hulls, corncobs, sawdust, grain dust or any combination thereof may be substituted for rice hulls.

Starch or polymer binders and other strengtheners may be added if desired without departing from the invention herein described.

CLAIMS

1. A method of manufacture of an absorbent composition comprising the steps of mixing clay with cellulosic material, pelletizing the mixture, drying the resultant pellets, and heating the pellets to a temperature of from 550°C to 1100°C.

2. A method according to Claim 1 wherein the pellets are heated to a temperature above 550°C for three hours.

3. A method according to claim 1 or claim 2 wherein the pellets are heated to temperature of from 800°C to 850°C for at least one hour.

4. A method according to any one of the preceding claims wherein said cellulosic material is fibrous.

5. A method according to any one of the preceding claims wherein said cellulosic material comprises rice hulls, wheat dust, grain dust, peanut hulls, corncobs or sawdust or any combination thereof.

6. A method according to any one of the preceding claims wherein the ratio of clay to cellulosic material is in the range of 86:14 by weight to 60:40 by weight.

7. A method according to any one of the preceding claims wherein the particle sizes of clay and cellulosic material prior to pelletizing is between 75 and 600 microns.

8. A method according to any one of the preceding claims wherein the pellets have a diameter on their longest axis of less than 10 m.m.

9. A method according to any one of the preceding claims

wherein the pellets are dried to a moisture content of less than 4% by weight.

10. A method according to any one of the preceding claims further including the step of combining a carbonate with the mixture prior to pelletizing.

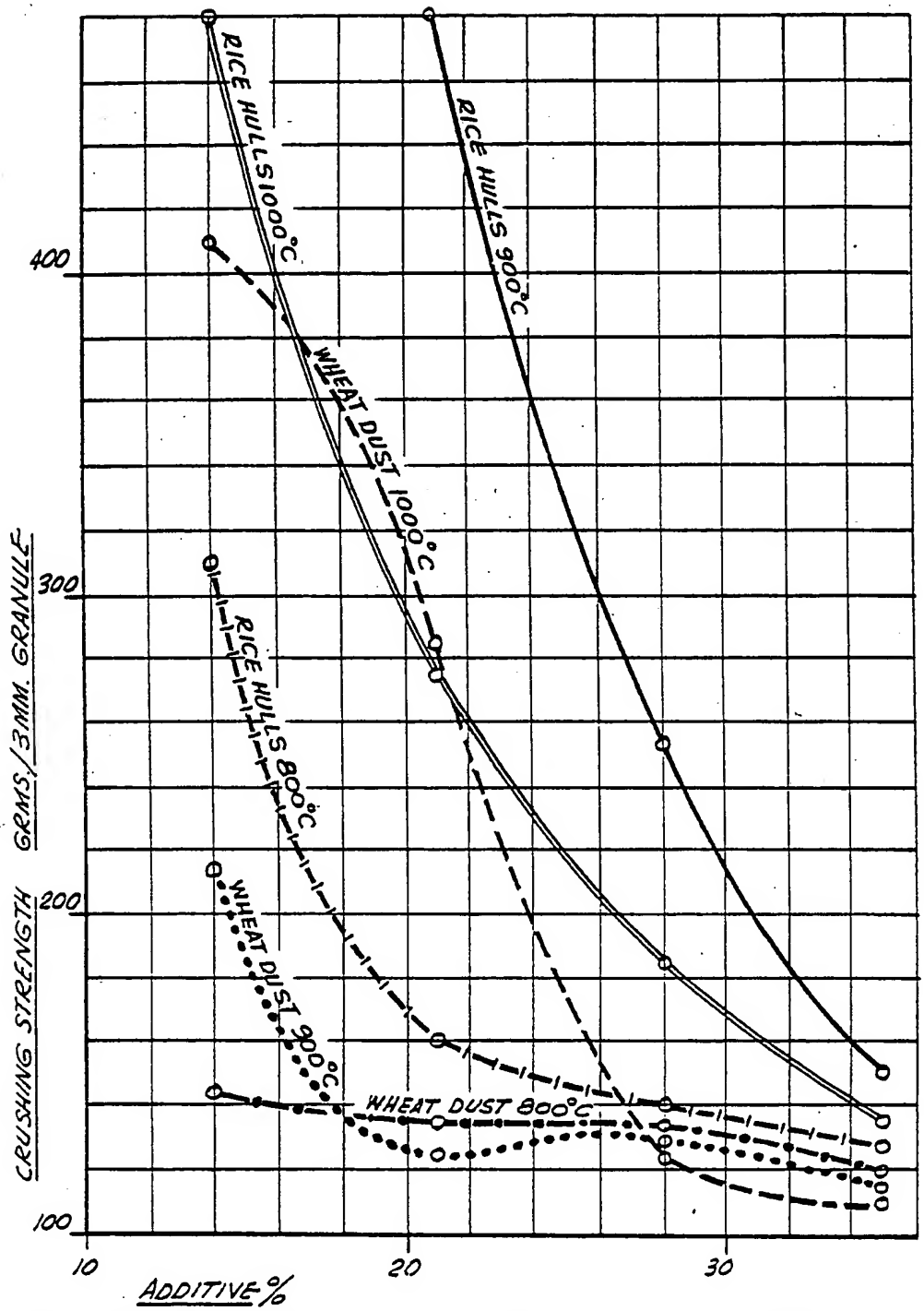
11. A method according to any one of the preceding claims wherein the pellets are heated to a temperature of from 800°C to 1000°C for a time sufficient to complete combustion of the cellulose and then cooled.

12. A method according to any one of the preceding claims wherein the pellets are formed by agglomeration in a granuation drum.

13. An absorbent composition when manufactured by a method according to any one of the preceding claims.

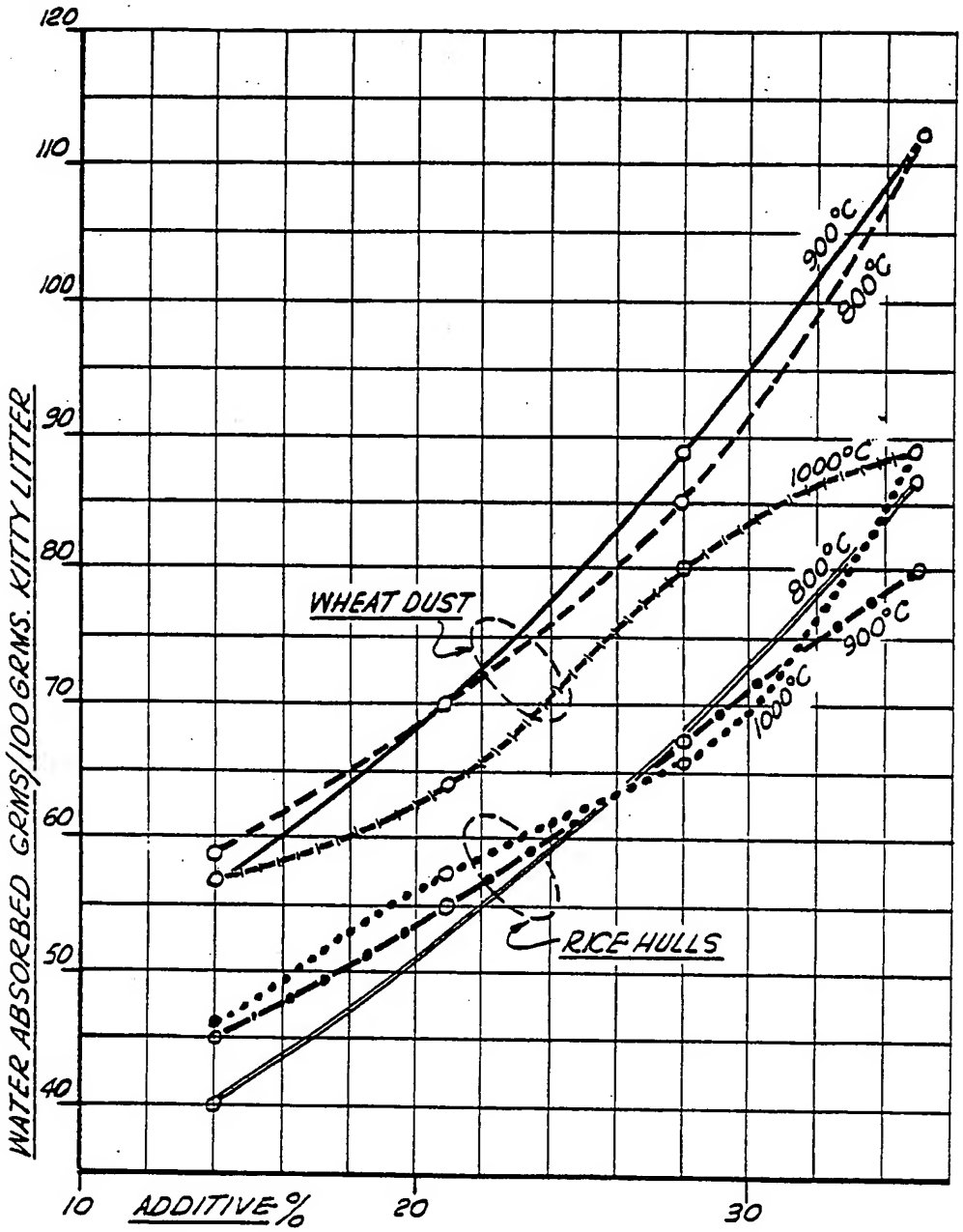
14. A method according to claim 1 substantially as herein described with reference to any one of the examples.

15. An absorbent composition substantially as herein described with reference to any one of the examples.



CRUSHING STRENGTH OF KITTY LITTER PREPARED FROM DIFFERENT ADDITIVES AND CALCINED AT DIFFERENT TEMPERATURES

FIG. 1



WATER ABSORPTION OF KITTY LITTER PREPARED FROM DIFFERENT ADDITIVES AND CALCINED AT DIFFERENT TEMPERATURES

FIG. 2

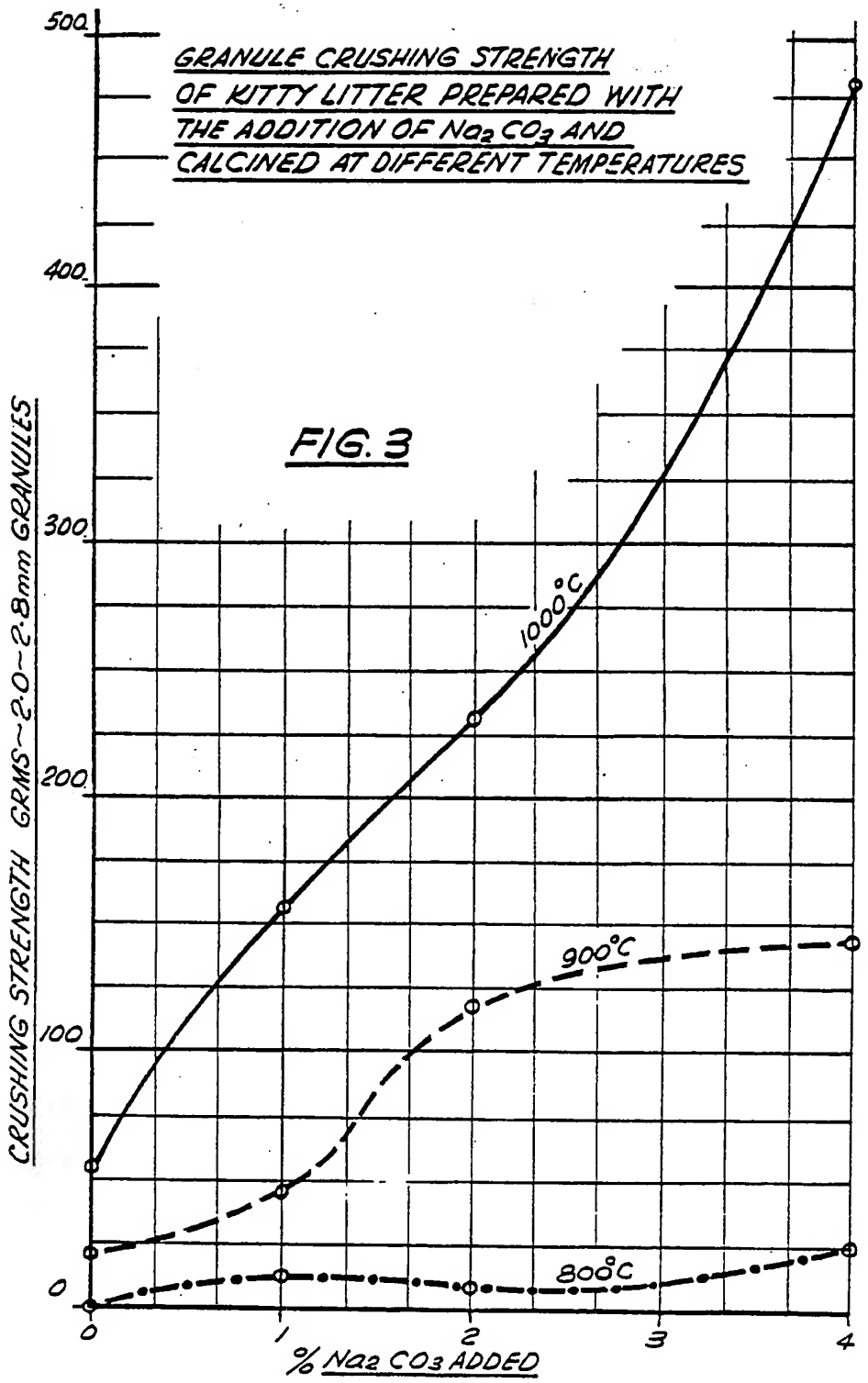

GRANULE CRUSHING STRENGTH
OF KITTY LITTER PREPARED WITH
THE ADDITION OF Na2 CO3 AND
CALCINED AT DIFFERENT TEMPERATURES
CRUSHING STRENGTH GRMS~2·0~2·8mm GRANULES
500
400
300
200
100
0
1000°C
900°C
800°C
0
1
2
3
4
% Na2 CO3 ADDED

FIG. 3

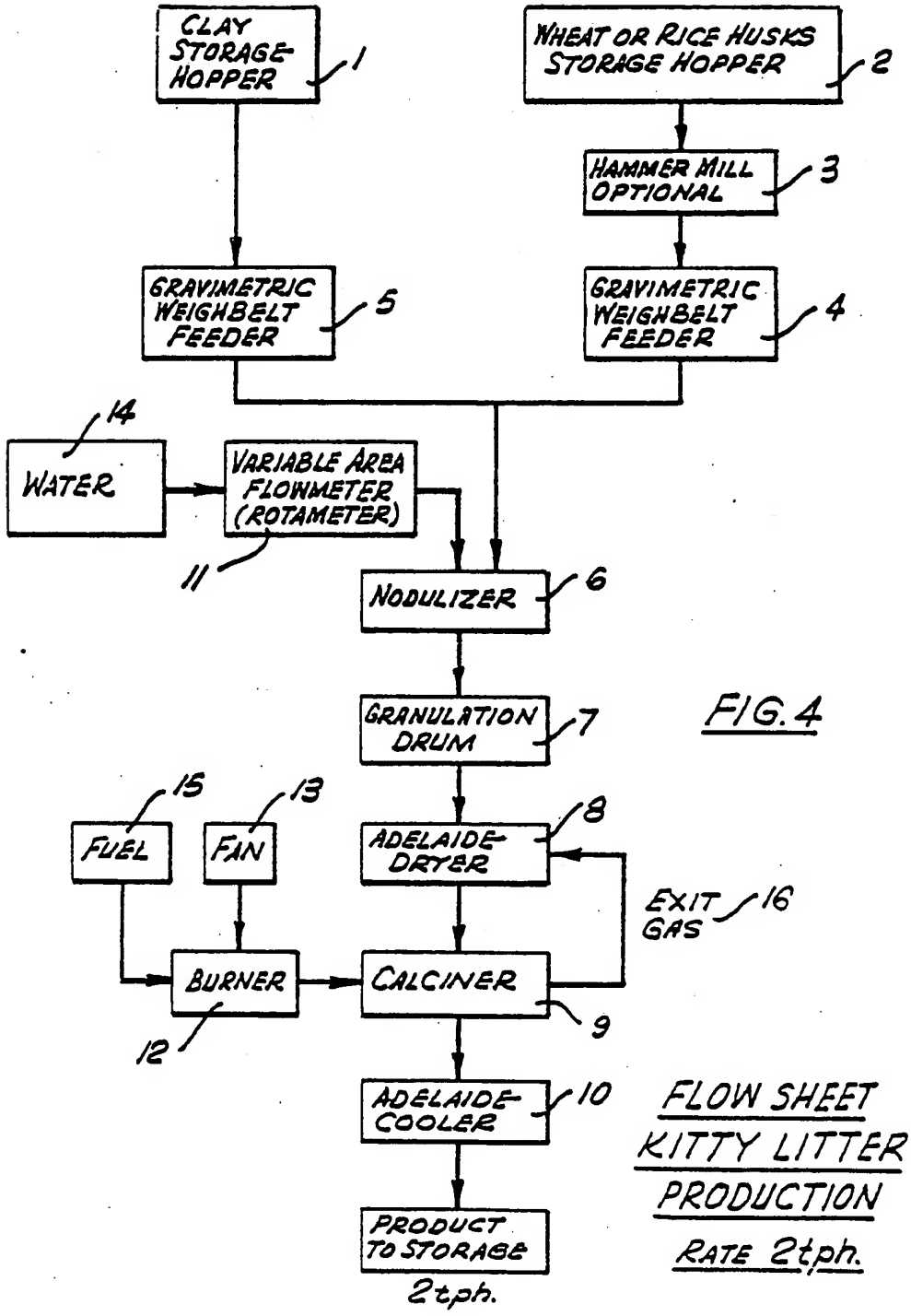


FIG. 4

FLOW SHEET
KITTY LITTER
PRODUCTION
RATE 2tph.

INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 85/00152

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.[4] A01K 1/01, 1/015 ,B01J 20/12, 20/30

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	B01J 1/22, 20/12, 20/30, A01K 1/01, 1/015
US Cl.	119-1

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

AU : IPC as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 4374044 (SCHAEFER et al) 15 February 1983 (15.02.83)	(1-15)
Y	US, A, 2470346 (FRANKENHOFF) 17 May 1949 (17.05.49)	(1-15)
Y	US, A, 3789797 (BREWER) 5 February 1974 (05.02.74)	(1-15)
Y	WO, A, 83/03255 (SKAMOL SKARREHAGE MOLERVAERK A/S) 29 September 1983 (29.09.83)	(1-15)
Y	AU, A, 53706/79 (ROCLA CONCRETE PIPES LTD) 7 August 1980 (07.08.80)	(1-15)
Y	DE, A, 2116435 (SKAMOL SKARREHAGE MOLERVAERK A/S) 4 November 1971 (04.11.71)	(1-15)

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
03 October 1985 (03.10.85)	(14-10-85) 14 OCTOBER 1985
International Searching Authority	**Signature of Authorized Officer**
AUSTRALIAN PATENT OFFICE	R.E. Grant (R.E. GRANT)

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 85/00152

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report	Patent Family Members			
US 4374044	CA 1165303	EP 57333	JP 57136939	
DE 2116435	DK 127410	GB 1330730		
WO 83/03255	DK 1059/82	EP 113729		

END OF ANNEX